The System CaO-CaF_2

TRYGGVE BÅÅK

Division of Metallurgy of Iron and Steel, Royal Institute of Technology, Stockholm, Sweden

In studies on the electrical conductivity of the system $CaO - CaF_2$ it has been shown that there exists a gap of miscibility in the liquid state on the CaF_2-rich side of the diagram.

Previously this system had only superficially been studied by Eitel [1] as part of a greater work with the method of thermal analysis. In his work, he reported a value for the eutectic point. However, Eitel did not use the highest grade of purity of CaF_2 and thus found a melting point for the fluoride which was too low. The true melting point has been determined by Naylor [2] and found to coincide with the one in this work.

The experiments were carried out in a high frequency furnace and the temperature was measured with a Pt : Pt—10 % Rh thermocouple. The resistances of the melts were measured between molybdenum electrodes, the cell constant of which was determined using 0.1 *N* KCl. The determinations were made in carbon crucibles with thoroughly weighed and blended mixtures of CaO and CaF_2, A.R. grade. All experiments were carried out in a purified nitrogen atmosphere. The carbide contamination from the carbon crucibles could be shown to be negligible with

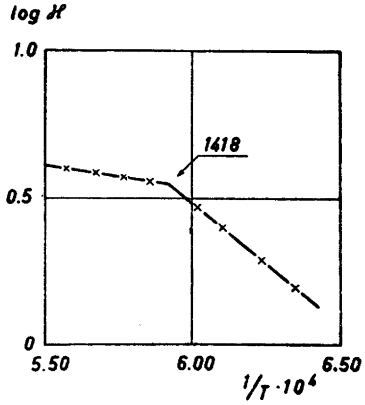

Fig. 1.

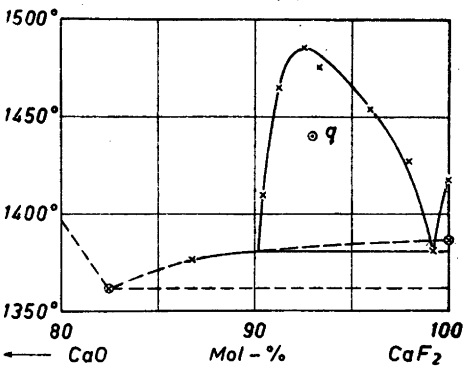

Fig. 2.

mixtures up to about 15 mol-% CaO. From measured values of the resistances, the conductivities ($\varkappa$) were computed in the usual way. Phase transitions are found as discontinuities in the curves of $\log \varkappa$ as a function of $1/T$. An example (pure CaF_2) of these curves is shown in Fig. 1. All results are summarised in the equilibrium diagram (Fig. 2), where crosses ($\times$) are from this investigation, while crosses with rings ($\oplus$) and the dotted lines are from Eitel. The diagram shows a gap of miscibility with a maximum at about 92.5 mol-% CaF_2 and 1 485° C. The gap goes from 0.8 mol-% to about 10 mol-% CaO.

The point *q* represents an experiment in which a mixture has first been heated to 1 510° C after which it has been cooled down to 1 440° C and kept at this temperature for two hours and then quenched. The result was two phases with a sharp boundary.

Finally, it may be remarked that the electrical conductivity of CaF_2 at the melting point (1 418° C), $\varkappa = 3.56\ \text{ohm}^{-1}\text{cm}^{-1}$, is of the same magnitude as that of $CaCl_2$, $\varkappa = 4.17\ \text{ohm}^{-1}\text{cm}^{-1}$, extrapolated to the same temperature [3].

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1. Eitel, W. *Zement* **27** (1938) 469.
2. Naylor, B. F. *J. Am. Chem. Soc.* **67** (1945) 150.
3. Drossbach, P. *Elektrochemie geschmolzener Salze*, Berlin, 1938, p. 72.

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